

of that date show that he proved thereby, and then, the practicability of precisely determining the form and limits of any storm. All that he asked of the Signal Service now was to make continuous observations, instead of three observations a day, and to put down upon their charts the other more important elements with that of barometric pressure.

Prof. Houston noticed the fact that, by the barometer at the High School, the mercury stood, on the 5th of February at 1.20 P. M., at the most extraordinary height of 30.94. He wished also to put on record his proposed improvement of the barometer, at the mechanical details of which he is now working, viz: to read with greater ease and precision, by means of a scale floated on the surface of the mercury, counterbalanced and connected with a ring around the tube.

Prof. Sadtler, by permission of the Geological Survey of Pennsylvania, gave the scientific results of his recent analyses of gas from several oil wells in Western Pennsylvania—gas which is used in the iron manufacture.

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CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.

No. VI.

*On the Composition of the Natural Gas from certain Wells in Western Pennsylvania.*

BY SAMUEL P. SADTLER.

(*Read before the American Philosophical Society, Feb. 18, 1876.*)

Having had occasion lately to analyse some of the gases issuing from wells in Western Pennsylvania, I have obtained some results which are given as a contribution to our knowledge of these important natural products. There have been almost no analyses whatever made of these gases. In 1866 a French geologist, M. Foncou visited a number of these gas-wells and collected specimens of the gases. These were afterwards analysed by M. Fonqué, and the results are published in *Compt. rendus LXVII. p. 1045*. The localities were Pioneer Run, Venango Co., Pa.; Fredonia, N. Y.; Roger's Gulch, Wirt Co., W. Va.; Burning Springs, on the Niagara river below the Cataract; and Petrolia, Enniskillen district, Canada West. These points are certainly widely enough removed to make the series comprehensive from a geological standpoint. The analyses do not appear to have been complete ones, as M. Fonqué determined the exact amounts of only a few of the constituents. In general, the gases were composed of

members of the marsh-gas series of hydrocarbons. Thus the gas from Pioneer Run he found to have essentially the composition of propyl hydride ( $C_3 H_8$ ), with small quantities of carbonic acid and of nitrogen; the Fredonia gas appeared to be a mixture of marsh-gas ( $CH_4$ ) and ethyl hydride ( $C_2 H_6$ ), with a small quantity of carbonic acid and 1.55 per cent. of nitrogen; the Rogers' Gulch gas was  $CH_4$  almost exclusively, with 15.86 per cent. of carbonic acid, and a small quantity of nitrogen; the Burning Springs gas almost pure  $CH_4$  with a little  $CO_2$ ; the Petrolia gas a mixture of marsh-gas ( $CH_4$ ) and ethyl hydride ( $C_2 H_6$ ), with a small amount of carbonic acid.

However, in some cases the composition as given above was only apparent, as in the case of the Pioneer Run gas, for on passing the gas through alcohol a part was absorbed, which was afterwards shown to be butyl hydride ( $C_4 H_{10}$ ), while the part unabsorbed showed nearly the composition of marsh-gas ( $CH_4$ ). It was evident, therefore, that what appeared to be propyl hydride ( $C_3 H_8$ ) was in reality a mixture of marsh-gas ( $CH_4$ ) and butyl hydride ( $C_4 H_{10}$ ).

In 1870, Prof. Henry Wurtz made an analysis of the gas from a well in West Bloomfield, N. Y. The results of this analysis are found in *Silliman's Journal* (2) *XLIX.*, p. 336. He found :

Marsh-gas.....	82.41
Carbonic acid.....	10.11
Nitrogen.....	4.31
Oxygen.....	0.23
Illuminating hydrocarbons.....	2.94

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100.00

The specific gravity of the gas was .693.

The methods of analysis were not the usual ones of gas-analysis, but some new absorption methods devised by himself in conjunction with Prof. B. Silliman. This, I believe, is the extent of the published information on the subject.

The gases which I collected and analyzed were :

First, the gas of the Burns Well in Butler County; secondly, that of the Harvey Well in the same county; thirdly, that from the Leechburg Well across the Kiskeminitis river from Leechburg, in Westmoreland County and fourthly, the gas bubbling from a spring at Cherry Tree in Indiana County. As the results of Fonqué just given had rendered the presence of higher members of the marsh-gas series than  $CH_4$  probable, at two of these wells, I made, in addition, absorption tests with absolute alcohol and with bromine, hoping to prove qualitatively the presence or absence of these higher hydrocarbons as well as those of the ethylene series. For while marsh-gas itself is insoluble in absolute alcohol, ethyl hydride ( $C_2 H_6$ ) is dissolved to the extent of  $1\frac{1}{2}$  volumes, propyl hydride ( $C_3 H_8$ ) to the extent of 6 volumes, and butyl hydride ( $C_4 H_{10}$ ) to the extent of 18 volumes in one volume of the alcohol. A pas-

sage of the natural gas for 15 or 20 minutes, therefore, should saturate the alcohol with such of these hydrocarbons as might be present. The bromine absorption test was made in order to ascertain whether any ethylene or butylene dibromide would be formed by the passage of gas.

The gases tested in this way were the gas from the Burns Well and gas from the Leechburg Well. The bottles containing the alcohol, having been tightly stoppered and sealed at the time, were afterwards examined in the Laboratory. The Burns Well gas was first examined. The alcohol through which the gas had been passed was transferred to a small flask, and enough additional alcohol was added to completely fill the flask. A cork perforated and carrying a delivery tube was then fitted to it so that the excess of alcohol filled this tube also.

The flask was now heated, and the gas given off was collected in a eudiometer tube over warm water. I obtained thus some 150 cubic centimeters of gas. The operation was pushed until only alcohol vapor was given off, which was absorbed by the water. To the gas in the eudiometer I then added rapidly an equal volume of chlorine, and allowed it to stand exposed to diffused sunlight. Oily drops formed at once, while the volume of the gas contracted until it occupied only about one-half of the first volume.

This showed the probable formation of ethyl chloride ( $C_2H_5Cl$ ) which is gaseous at temperatures over  $12^{\circ}C$ , and of either propyl chloride ( $C_3H_7Cl$ ) which is liquid at temperatures under  $52^{\circ}C$ , or of butyl chloride ( $C_4H_9Cl$ ) which is liquid at temperatures under  $77.6^{\circ}C$ . On inverting and applying a flame to the gas in the eudiometer, it was found to be inflammable, burning with the greenish flame characteristic of ethyl chloride. The water upon which the oily drops had collected, was put in a small flask, and an attempt was made to separate them by distillation. This was however, unsatisfactory, as there could only have been small quantities of either propyl chloride or butyl chloride. The water in the eudiometer tube reacted acid from the  $HCl$  formed.

The result of these tests may therefore be summed up as showing the certain presence in the gas of ethyl hydride ( $C_2H_6$ ) and the probable presence of either  $C_3H_8$  or  $C_4H_{10}$ .

The qualitative examination of the Leechburg gas was made in the same way. I obtained here only about 100 cubic centimeters of gas on heating the alcohol. On mixing with chlorine a contraction of about one-third took place. The inflammability of the residual gas and the formation of oily drops gave the same indications as with the other gas.

The other qualitative tests were with bromine. This had been tightly bottled and sealed up. The bromine from the test with the Burns gas was then placed in a porcelain dish and water added. Pure sodic hydrate was added to neutralize the excess of bromine. The sodium bromide formed dissolved at once in the water. There remained no trace of oily drops such as would be caused by the bromides of the olefine series of hydrocarbons. The sodium bromide was afterwards crystallized out perfectly pure. The test was therefore entirely negative in its results.

On examining the bromine used for absorption with the Leechburg gas, there was apparently a slight layer upon the surface of the bromine, which might have been ethylene bromide. On neutralizing the excess of bromine, however, no distinct evidence could be had of the presence of the bromide, so that the result was left uncertain.

The quantitative analyses were next made. In these the carbonic acid, carbonic oxide, illuminating hydrocarbons, and free oxygen were tested for and when present removed by suitable absorption re-agents, while the hydrogen, marsh-gas and ethyl hydride were determined by the eudiometer analysis. Any nitrogen present remains over and is estimated at the conclusion of the analysis.

*Burns Well Gas* (average of two analyses).

Carbonic Acid.....	.34
Carbonic oxide .....	trace
Illuminating hydrocarbons ( $C^n H_{2n}$ ).....	—
Hydrogen.....	6.10
Marsh-gas ( $CH_4$ ).....	75.44
Ethyl-hydride ( $C_2 H_6$ ).....	18.12
Propyl-hydride ( $C_3 H_8$ ).....	trace
Oxygen.....	—
Nitrogen.....	—
	<hr/>
	100.00

*Leechburg Gas* (average of two analyses).

Carbonic acid.....	.35
Carbonic oxide.....	.26
Illuminating hydrocarbons ( $C_n H_{2n}$ ).....	.56
Hydrogen.....	4.79
Marsh-gas.....	89.65
Ethyl-hydride.....	4.39
Propyl-hydride.....	trace
Oxygen.....	—
Nitrogen.....	—
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	100.00

*Harvey Well Gas.*

Carbonic acid.....	.66
Carbonic oxide.....	trace
Illuminating hydrocarbons.....	—
Hydrogen.....	13.50
Marsh-gas.....	80.11
Ethyl-hydride.....	5.72
Propyl-hydride.....	trace
Oxygen.....	—
Nitrogen.....	—
	<hr/>
	99.99

*Cherry Tree Gas* (average of two analyses).

Carbonic acid.....	2.28
Carbonic oxide.....	—
Illuminating hydrocarbons.....	—
Hydrogen.....	22.50
Marsh-gas.....	60.27
Ethyl-hydride.....	6.80
Oxygen.....	.83
Nitrogen.....	7.32
	<hr/>
	100.00

It will be seen that the first three of the gases just analyzed are very similar in composition, while the gas escaping from the spring at Cherry Tree differs very considerably from the others. The larger amount of carbonic acid and the presence of free oxygen and nitrogen are the chief points which distinguish it. It is only natural, however, that a gas escaping from fresh spring water should contain these gases, as they are the gases usually dissolved in spring water. As to the other constituents of these gases, hydrogen, marsh-gas, and ethyl hydride are the most important ones. In the case of two of the gases, the Burns gas and the Leechburg gas, qualitative tests directly proved the presence of this last constituent. The other two ingredients can also be proved to be there by the application of Bunsen's formulas to the result of the eudiometric analysis. Thus, as the volume of gas taken for the eudiometric analysis can contain only hydrogen, hydrocarbons of the marsh-gas series and nitrogen, we need for our formulas four known values; the volume taken, the contraction after passage of the spark, the carbonic acid produced by the combustion and the free nitrogen in the sample of gas taken.

In the three gases first analyzed this last constituent proved to be absent, so that we had only three values, and could form only three equations, containing three unknown quantities. These equations were:

$$\begin{aligned} x + y + z &= V. (1). \\ y + 2z &= C. (2). \\ 3x + 2y + \frac{5}{2}z &= A. (3). \end{aligned}$$

where  $V$  equals the volume taken,  $C$  the carbonic acid formed, and  $A$  the absorption or contraction, consequent upon the explosion, where also  $x$  was taken as hydrogen ( $H_2$ ),  $y$  was taken as marsh-gas ( $CH_4$ ), and  $z$  was taken as ethyl-hydride ( $C_2H_6$ ). When in these equations were substituted the found values of  $C$  and  $A$ , I got plus values for  $x$ ,  $y$ , and  $z$ . On the other hand, if I assumed two constituents only,  $x$  as hydrogen and  $y$  as marsh-gas, the  $y$  was made equal to  $C$  at once, which was obviously incorrect, and would have given a minus value to  $x$ . If again, I assumed  $x$  to be equal to  $CH_4$ , and  $y$  equal to  $C_2H_6$ , I got false values for  $x$  and  $y$ . One other assumption only was open to me, that was to take  $x$  as hydrogen,  $y$  as marsh-gas ( $CH_4$ ), and  $z$  as propyl hydride ( $C_3H_8$ ). This would have given

plus values for  $x$ ,  $y$ , and  $z$ , but the previous qualitative tests had shown conclusively the presence of  $C_2 H_6$ .

I found, however, unexpectedly in Fonqué's memoir the strongest confirmation of my interpretation of my results. Using the three equations that I have given above, he finds that when  $x$ ,  $y$ , and  $z$  represent three successive members of the marsh-gas series, the equations are as follows:

$$x + y + z = V. (1).$$

$$x + 2y + 3z = C. (2).$$

$$2x + \frac{5}{2}y + 3z = A. (3).$$

from which can be deduced as a fourth equation.

$$2A - 3V = C. (4).$$

In other words, when an eudiometric analysis of a mixture of hydrocarbons of the marsh-gas series is made, the carbonic acid formed is equal to twice the contraction, minus three times the volume of gas taken.

He says, therefore, (*Compt. rendus*. LXVII. p. 1048) when the marsh-gas hydrocarbons are mixed with free hydrogen, this fourth equation is not realized. I did not find it realized in any of my analyses. Thus in the analyses of the Burns Well gas, I had the following figures :

	I.	II.
Gas taken.....	32.74	24.49
Contraction.....	70.4	52.75
CO <sub>2</sub> absorbed.....	36.6	27.5

If we substituted the values of C and V as found, in the formula  $2A = C + 3V$ , we get, for the first,  $36.6 + 98.22 = 134.82$ , of which the half is 67.41. But the observed contraction is 70.4, or 2.99 greater than that demanded by Fonqué's formula for the marsh-gas hydrocarbons. So for the second we get  $27.5 + 73.47 = 100.97$ , of which the half is 50.485, while the observed contraction is 52.75.

If now we turn to to the formulas first stated by me, we find the explanation in the third equation where we have  $3x$ , assuming  $x$  to be hydrogen ; and in the second equation where we have  $0x$ , assuming  $x$  to be hydrogen.

I have not been able as yet to make any experimental determinations of the specific gravity of these gases, but have the material reserved, and expect to do so. The specific gravities as calculated from the analyses given, are as follows :

	Sp. gr.
Burns Well gas.....	.6148

Mr. Lesley mentioned that Mr. Hall had found three casts of an *Orthis* of the Trenton (Bala) Limestone in a sub-angular fragment among the moraine (?) matter cut into for a drain in front of the University buildings in West Philadelphia.

Mr. McArthur presented through Mr. Walter nine photographs of models of ornaments for the Public Buildings.

Pending nomination No. 791 and new nomination No. 792 were read.

The minutes of the last meeting of the Board of Officers and Council were read.

Mr. Blodget, from the Committee on the Progress of Science Exhibition at the Centennial, reported that his Committee had met, and would act with a committee appointed by the Acad. Nat. Science, Phila. (Dr. Le Conte, Mr. C. E. Smith, Mr. W. Vaux), and he read a paper expressing the views of the joint committee, and explained that a room 24' by 48' in the southeast end of the Main Building, up-stairs, had been appropriated by the Commission to their use, and there was good reason to believe that learned Societies would respond cordially enough to fill this room.

Prof. Campbell disclaimed for the Commission all responsibility, except for guaranteeing the right of placing whatever it saw fit in this room by the joint committee.

Prof. Fraley said that an application would be made to the Society for permission to exhibit its Elliot Bible.

There being no other business, the meeting adjourned.

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*Stated Meeting, March 3, 1876.*

Present, 10 members.

Mr. Eli K. Price in the Chair.

Letters of acknowledgment were received from Dr. Jacob Bigelow (95); Silliman's Journal (95); the Smithsonian Institution (95); the Emden Society (92); and the Physical Society in Berlin (87 to 91; xiv, 3, xi, 1).

Letters of envoy was received from the Coast Survey; from the Physical Society in Berlin; and from the

Royal Irish Society, requesting missing Parts 2 of Vol. iii, 1